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(54) Title: PACKAGING OF RESPIRING BIOLOGICAL MATERIALS

(57) Abstract: Packaging of respiring biological materials, particularly bananas and other fruits, in sealed containers. The containers preferably include a gas-permeable membrane comprising (1) a microporous film, and (2) a polymeric coating on the microporous film. Using appropriate containers and appropriate controlled atmospheres around the container, the respiring materials can be stored and/or ripened under controlled conditions. Bananas can be ripened while they are being transported, or in conventional ripening rooms without opening the containers in which they have been transported. The ripe bananas are less dehydrated and remain in a satisfactory ripened state for longer periods of time.

PACKAGING OF RESPIRING BIOLOGICAL MATERIALS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of copending, commonly assigned, U.S. Application Serial No. 09/989,682,filed November 20, 2001, which is a continuation-in-part of copending, commonly assigned U.S. Application Serial No. 09/858,190, filed May 15, 2001, which claims priority under 37 CFR 1.78 (a) (5) from Provisional Application Serial No. 60/325,762. Provisional Application Serial No. 60/325,762 has an effective filing date of May 26, 2000, and resulted from the conversion to a provisional application of Application Serial No. 09/580,379, filed May 26, 2000. This application is related to International Patent Application No. PCT/U.S. 01/40732, which was filed on May 15, 2001, claiming U.S. priority of May 26, 2000. International Patent Application No. PCT/U.S. 01/40732 was published as International Publication No. W0 01/91211/8 on Dec. 6, 2001, i.e. after the priority date of this application, November 20, 2001.

BACKGROUND OF THE INVENTION

This invention relates to the packaging of respiring biological materials.

Respiring biological materials, e.g. fruits and vegetables, consume oxygen (O_2) and produce carbon dioxide (CO_2) at rates which depend upon the stage of their development, the atmosphere surrounding them and the temperature. In modified atmosphere packaging (MAP), the objective is to produce a desired atmosphere around respiring materials by placing them in a sealed container whose permeability to O_2 and CO_2 is correlated with (i) the partial pressures of O_2 and CO_2 in the air outside the package, and (ii) the temperature, to produce a desired atmosphere within the container. In many cases, the container includes an atmosphere control member having a high permeability to O_2 and CO_2. In controlled atmosphere packaging (CAP), the objective is to produce a desired atmosphere around respiring materials by displacing some or all of the air within a container by one or more

gases, e.g. nitrogen, O_2, CO_2 and ethylene, in desired proportions. Reference may be made, for example, to U.S. Patent Nos. 3,360,380 (Bedrosian), 3,450,542 (Badran), 3,450,544 (Badran et al.), 3,798,333 (Cummin et al), 3,924,010 (Erb), 4,003,728 (Rath), 4,734,324 (Hill), 4,779,524 (Wade), 4,830,863 (Jones), 4,842,875 (Anderson), 4,879,078 (Antoon), 4,910,032 (Antoon), 4,923,703 (Antoon), 4,987,745 (Harris), 5,041,290 (Wallace et al.) 5,045,331 (Antoon), 5,063,753 (Woodruff), 5,160,768 (Antoon), 5,254,354 (Stewart), 5,333,394 (Herdeman), 5,433,335 (Raudalus et al.), 5,460,841(Herdeman), 5,556,658 (Raudalus et al.), 5,658,607 (Herdeman), 6,013,293 (De Moor) and 6,376,032 (Clarke et al), International Publication Nos. WO 94/12040 (Fresh Western) and WO 00/04787 (Landec), and European Patent Applications Nos. 0,351,115 and 0,351,116 (Courtaulds). The disclosure of each of these patents and publications is incorporated herein by reference.

The preferred packaging atmosphere for a respiring material often depends on the age of the material and the changes (if any) in the material which are desired. Generally, for example, the preferred O_2 content during storage of unripe fruits is lower than the preferred O_2 content during subsequent ripening at a higher temperature. This fact causes problems for both MAP and CAP. For example, in MAP, although the O_2 permeability of the container generally increases with temperature (especially if it contains an atmosphere control member comprising a crystalline polymer having an appropriate melting point, as disclosed in U.S. Patent No. 6,376,032 and International Publication No. W0 00/04787), the increase is often insufficient to avoid the need for significant compromise between the preferred atmospheres at different stages. In CAP, it is theoretically possible to monitor the packaging atmosphere and to change it as often as is necessary to maintain the preferred level of O_2 (and other gases). But this is difficult and expensive, and often impractical.

Many fruits are picked when they are unripe; transported and stored under conditions which prevent or retard ripening; and ripen shortly before sale. Many fruits ripen more rapidly when exposed to ethylene, and some (e.g. bananas, tomatoes, avocados, Bartlett pears, kiwis, melons, peppers and mangos) are ripened commercially by exposure to ethylene in ripening rooms. When the fruits have been placed in a sealed bag or other container for transport or storage, the container is opened to expose the fruits to the ethylene. Another problem associated with the use of ripening rooms is that the fruits can ripen too rapidly, especially when the fruits ripen through a climacteric and therefore undergo a very large increase in respiration rate and generate heat in the ripening room.

As explained in U.S. Serial No. 09/989,682 and International Publication No. W0 01/912118, conventional procedures for the transport, storage and ripening of bananas

suffer from a number of problems which can be mitigated or overcome by the invention described in those applications.

SUMMARY OF THE INVENTION

A first area of the present invention is applicable to all respiring biological materials (including but not limited to bananas and other fruits which can be ripened by exposure to ethylene) and is concerned with situations in which the preferred packaging atmosphere has a relatively low O_2 content during one stage and a relatively high O_2 content during another stage. In this area of the invention, valuable results are obtained by combining the techniques of MAP and CAP. For example, a container having a high O_2 permeability can be placed either (i) in air when a packaging atmosphere of high O_2 content is desired, or (ii) in a controlled atmosphere having a selected reduced O_2 content when a packaging atmosphere of low O_2 content is desired.

A second area of the present invention is the application of the teachings of U.S. Serial No. 09/858,190 and International Patent Application No. PCT/US 01/40732 (1) not only to bananas, but also to other fruits which can be ripened by exposure to ethylene, and (2) to the ripening of bananas and other fruits by exposing them to gaseous ripening agents other than ethylene.

The first and second areas of the invention can be combined.

Some fruits generate ethylene as they ripen. Such ethylene is referred to herein as endogenous ethylene. The term "exogenous ethylene" is used herein to mean ethylene which is not derived from the fruits which are being ripened. Some other materials, for example acetylene, will also assist ripening of fruits which are ripened by exposure to ethylene. Reference may made for example to Burg,et al, Molecular Requirements for the Biological Activity of Ethylene, Plant Physiol (Lancaster) (1967) 42: 144-155, the disclosure of which is incorporated herein by reference. The term "ethylenic ripening agent" is used herein to mean ethylene or another substance which also assists ripening of fruits which can be ripened by exposure to ethylene. The abbreviation ERA is used herein for the term "ethylenic ripening agent". The term "exogenous ERA" is used herein to mean ethylenic ripening agent which is not derived from the fruits which are being ripened.

The first area of the invention includes the following Aspects I and II.

<u>Aspect I.</u> A method of treating, e.g. storing and/or ripening, a respiring biological material, the method comprising

(A) providing a sealed package comprising

(a) a sealed container, and

(b) within the sealed container, the respiring biological material and a packaging atmosphere around the respiring biological material;

the sealed container providing a pathway for O_2 and CO_2 to enter or leave the packaging atmosphere;

(B) exposing the exterior of the sealed package to a first controlled atmosphere;

(C) after step (B), exposing the exterior of the sealed package to a second controlled atmosphere;

the difference between the O_2 contents of the first and second controlled atmospheres being at least 1%, preferably at least 3%. The term "controlled atmosphere" is used herein to denote any atmosphere whose content is known. Thus, the term includes air and any atmosphere produced by adding known amounts of further gases to an existing controlled atmosphere (including the addition of additional quantities of a gas already present in the existing atmosphere), the further gases being added directly to the atmosphere (i.e. not passing through a permeable body before reaching the atmosphere).

In one embodiment of the method of Aspect I,

(a) in step (B), the first controlled atmosphere has an O_2 content which is (i) less than 18% O_2, preferably less than 12% O_2, particularly less than 9% O_2, and (ii) more than 2% O_2, preferably more than 4% O_2, particularly more than 5% O_2, and

(b) in step (C), the second controlled atmosphere contains at least 3% more O_2 than the first atmosphere.

In another embodiment of the method of Aspect I,

(a) at the beginning of step (B), the fruits are unripe fruits which ripen when exposed to an ethylenic ripening agent (ERA), for example green bananas;

(b) the O_2 content of the first controlled atmosphere and the permeability of the container are such that the O_2 content of the packaging atmosphere during step (B) is high enough to maintain respiration of the unripe fruits and low enough that the unripe fruits ripen slowly or not at all; and

(c) the second controlled atmosphere contains exogenous ERA, for example exogenous ethylene.

In another embodiment of the method of Aspect I, the first controlled atmosphere is air, and the second controlled atmosphere contains at least 3% more oxygen than the first atmosphere, and preferably has an O_2 content of at least 24%, particularly at least 28%.

In another embodiment of the method of Aspect I,

(a) at the beginning of step (B), the fruits are unripe fruits which can be ripened by exposure to ethylene, for example green bananas;

(b) the sealed container contains a latent source of exogenous ERA;

(c) at least the initial part of step (B) is carried out under conditions such that ERA is not released from the latent source; and

(d) during or after step (B), the latent source of exogenous ERA is activated, thereby releasing exogenous ERA which ripens the fruits.

In another embodiment of the method of Aspect I,

(a) at the beginning of step (B), the fruits are unripe fruits which can be ripened by exposure to ethylene, for example green bananas;

(b) during at least part of step (B), the first controlled atmosphere contains at least 23% O_2, preferably 25-30% O_2, e.g. about 28% O_2, and exogenous ERA, for example at least 20 ppm, e.g. 100 to 3000 ppm, of ethylene; and

(c) during at least part of step (C, the second controlled atmosphere contains 18 to 22% O_2 , for example is air.

In this embodiment, the O_2 content of the packaging atmosphere can be, for example, 4 to 8%, preferably 5.5 to 6.5%, during at least part of step (B), and 2 to 4%, preferably 2.5 to 3.5%, during at least part of step (C)

In another embodiment of the method of Aspect I,

(a) the second controlled atmosphere contains (i) less than 18% O_2, preferably less than 12% O_2, particularly less than 9% O_2, and (ii) more than 2% O_2, preferably more than 4% O_2, particularly more than 5% O_2; and

(b) has an O_2 permeability such that, during at least one period of step (B), the O_2 content of the packaging atmosphere reaches a value which is (i) more than 1%, preferably more than 2%, and (ii) less than 7%, preferably less than 5%, particularly less than 3.5%.

<u>Aspect II.</u> A container system suitable for carrying out the method of Aspect I or which has been used to carry out the method of Aspect I, the system comprising

(1) a sealed enclosure, for example a shipping or trucking container or a ripening room having an inlet port;

(2) within the enclosure, a plurality of sealed packages as defined in Aspect I; and

(3) a source of O_2 connected to the inlet port, whereby the sealed packages can be surrounded by a controlled atmosphere having a desired O_2 content.

This system is particularly useful for the transport and/or storage and/or ripening of bananas.

When the sealed packages contain unripe fruits which can be ripened by exposure to ethylene, the sealed enclosure preferably includes a second inlet port and a source of exogenous ERA connected to the second inlet port. Alternatively or additionally, within the sealed enclosure, there is a latent source of exogenous ERA, or a source of exogenous ERA, or the residue of a source of exogenous ERA.

In the first area of the invention, the container preferably includes at least one atmosphere control member which provides a pathway for O_2 and CO_2 to enter or leave the packaging atmosphere and which comprises a gas-permeable membrane comprising (i) a microporous polymeric film, and (ii) a polymeric coating on the microporous film. However, the container can be one which does not include an atmosphere control member, for example a polyethylene bag of the kind conventionally used for shipping bananas, whose O_2 permeability is too small to permit satisfactory ripening in a conventional ripening room.

The second area of the present invention includes the following aspects III to IX.

<u>Aspect III.</u> A package which comprises

(a) a sealed container, and

(b) within the sealed container, unripe fruits which can be ripened by exposure to an ethylenic ripening agent (ERA), and a packaging atmosphere around the unripe fruits;

the sealed container having one or both of the following characteristics (A) and (B);

(A) it has an O_2 permeability at 13 °C, per kg of fruits in the container (OP13/kg), of at least 700, preferably at least 1000, particularly at least 1500, ml/atm.24 hrs and an R ratio at 13 °C of at least 1.3, preferably at least 2, more preferably at least 3; and

(B) it includes at least one atmosphere control member which provides a pathway for O_2 and CO_2 and ERA to enter or leave the packaging atmosphere and which comprises a gas-permeable membrane comprising (i) a microporous polymeric film, and (ii) a polymeric coating on the microporous film.

In one embodiment of Aspect III, the sealed container contains a latent source of ERA or a source of ERA.

<u>Aspect IV.</u> A package as defined in Aspect III, except that the unripe fruits have been ripened, and the sealed container contains the residue of a source of ERA.

In Aspects III and IV, the container preferably has an ERA permeability at 13 °C, per kg of fruits in the container (ERAP13/kg) which is at least 2 times, preferably least 3 times, more preferably at least 4 times, the OP13/kg of the container. In one embodiment, the fruits are unripe fruits which ripen through a climacteric, and have not yet reached their

climacteric; and the packaging atmosphere contains at least 0.8%, preferably 1.5 to 6%, especially 1.5 to 3%, of O_2, and less than 15%, preferably less than 7%, of CO_2, with the total quantity of O_2 and CO_2 being less than 16%, preferably less than 10 %. at least 10%, whereby the fruits are maintained in an unripe state. In another embodiment, the fruits are unripe fruits which ripen through a climacteric, and have reached their climacteric; and the packaging atmosphere contains at least 12%, particularly 14 to 19%, of O_2, and less than 10%, preferably less than 4%, of CO_2, with the total quantity of O_2 and CO_2 being less than 20 %, preferably less than 17%. The sealed container may for example contain at least 4 kg, preferably least 15 kg, especially 16 to 22 kg, of fruits.

<u>Aspect V</u> A method of ripening unripe fruits which comprises

(A) providing a sealed package as defined in Aspect III above; and

(B) placing the sealed package in an atmosphere containing ERA, for example in a ripening room containing ethylene, preferably in amount at least 20 ppm, for example 300 to 1000 ppm.

In one embodiment of the method of Aspect V, at least part of step (B) is carried out at a temperature less than 22 °C, preferably less than 20 °C, for example at 16-21°C.

In another embodiment of the method of Aspect V, the unripe fruits ripen through a climacteric and the packaging atmosphere, for at least part of the period before the fruits reach their climacteric, contains at least 10% preferably at least 12%, particularly 14 to 19%, of O_2, and less than 10%, preferably less than 4%, of CO_2, the total quantity of O_2 and CO_2 being less than 20 %, preferably less than 17%.

In another embodiment of the method of Aspect V, the packaging atmosphere, for at least part of the period after the fruits have passed their climacteric, contains at least 0.8%, preferably 1.5 to 6%, especially 1.5 to 3%, of O_2, and less than 15%, preferably less than 7%, of CO_2, the total quantity of O_2 and CO_2 being less than 16%, preferably less than 10%.

<u>Aspect VI.</u> A method of ripening unripe fruits which comprises

(A) providing a sealed package as defined in Aspect III wherein the sealed container also contains a latent source of exogenous ERA or a source of exogenous ERA, and

(B) exposing the unripe fruits in the sealed package to ERA from the source of exogenous ERA in the sealed container.

<u>Aspect VII</u> A sealed package which comprises

(a) a sealed container, and

(b) within the sealed container, (i) fruits, for example fruits which have ripened through a climacteric, (ii) a packaging atmosphere around the fruits, and (iii)

exogenous ERA and/or a residue of exogenous ERA and/or the residue of a source of exogenous ERA, the exogenous ERA and/or residue of exogenous ERA optionally being a gas which is part of the packaging atmosphere;

the sealed container providing a pathway for O_2, CO_2 and ERA to enter or leave the packaging atmosphere.

Aspect VIII A package which comprises

(a) a container, the container being a sealed container or an open container obtained by opening a sealed container, and

(b) within the container, (i) fruits, and (ii) a packaging atmosphere around the fruits; the container, if it is sealed, providing a pathway for O_2, CO_2 and ERA to enter or leave the packaging atmosphere, and if it is open, having provided a pathway for O_2 ,CO_2 and ERA to enter or leave the packaging atmosphere when it was sealed; the container having one or both of the following characteristics

(i) the fruits therein have been ripened at least in part by exposure to exogenous ERA, and

(ii) it contains the residue of a source of exogenous ERA.

For example, the container can be a sealed or open container in which the fruits have ripened through a climacteric as a result of exposure to ethylene in a ripening room, or as a result of exposure to exogenous ERA generated within the container while it was sealed.

Aspect IX. An enclosure, for example a shipping or trucking container, or a ripening room, which contains a plurality of sealed packages, each of the packages comprising

(a) a sealed container, and

(b) within the sealed container, (i) fruits, for example fruits which have ripened through a climacteric, or unripe fruits which ripen through a climacteric, and (ii) a packaging atmosphere around the fruits;

the sealed container providing a pathway for O_2, CO_2 and ERA to enter or leave the packaging atmosphere;

the enclosure containing the plurality of sealed packages having at least one of the following features

(i) the packaging atmosphere in each of the sealed packages contains exogenous ERA;

(ii) at least some, and preferably each, of the sealed packages contains exogenous ERA and/or a residue of exogenous ERA, the exogenous ERA and/or residue of exogenous ERA optionally being a gas which is part of the packaging atmosphere, and

(iii) the enclosure contains not only the sealed packages containing the fruits but also, not within any of the sealed packages, exogenous ERA and/or a residue of exogenous ERA, the exogenous ERA and/or residue of exogenous ERA optionally being a gas which is part of the atmosphere which contacts the exterior of the sealed packages.

DETAILED DESCRIPTION OF THE INVENTION

In the Summary of the Invention above and in the Detailed Description of the Invention, the Example, and the Claims below, reference is made to particular features (including method steps) of the invention. It is to be understood that the disclosure of the invention in this specification includes all possible combinations of such particular features. For example, where a particular feature is disclosed in the context of a particular aspect or embodiment of the invention, or a particular claim, that feature can also be used, to the extent possible, in combination with and/or in the context of other particular aspects and embodiments of the invention, and in the invention generally.

The term "comprises" and grammatical equivalents thereof are used herein to mean that other components, ingredients, steps etc. are optionally present. For example, an article " comprising" (or "which comprises") components A, B and C can consist of (i.e. contain only) components A, B and C, or can contain not only components A, B and C but also one or more other components. Where reference is made herein to a method comprising two or more defined steps, the defined steps can be carried out in any order or simultaneously (except where the context excludes that possibility), and the method can include one or more other steps which are carried out before any of the defined steps, between two of the defined steps, or after all the defined steps (except where the context excludes that possibility). The term "at least" followed by a number is used herein to denote the start of a range beginning with that number (which may be a range having an upper limit or no upper limit, depending on the variable being defined). For example "at least 1" means 1 or more than 1. The term "at most" followed by a number is used herein to denote the end of a range ending with that number (which may be a range having 1 or 0 as its lower limit, or a range having no lower limit, depending upon the variable being defined). For example, "at most 4" means 4 or less than 4, and "at most 40%" means 40% or less than 40 %. When, in this specification, a range is given as " (a first number) to (a second number)" or "(a first number) - (a second number)", this means a range whose lower limit is the first number and

whose upper limit is the second number. For example, 25-100 mm means a range whose lower limit is 25 mm, and whose upper limit is 100 mm.

In describing and claiming the invention below, the following abbreviations, definitions, and methods of measurement (in addition to those already given) are used. OTR is O_2 permeability. COTR is CO_2 permeability. EtTR is ethylene transmission rate. ERATR is ERA transmission rate. OTR, COTR, EtTR and ERATR values are given in ml/m^2.atm.24 hrs; in some cases, the equivalent in cc/100 inch^2.atm.24 hrs is given in parentheses. OTR and COTR values referred to herein can be measured using a permeability cell (supplied by Millipore) in which a mixture of O_2, CO_2 and helium is applied to the sample, using a pressure of 0.7 kg/cm^2 (10 psi) except where otherwise noted, and the gases passing through the sample were analyzed for O_2 and CO_2 by a gas chromatograph. The cell could be placed in a water bath to control the temperature. The abbreviation P_{10} is used to mean the ratio of the oxygen permeability at a first temperature T_1°C to the oxygen permeability at a second temperature T_2, where T_2 is $(T_1$-10)°C. T_1 being 10 °C and T_2 being 0 °C unless otherwise noted. The abbreviation R or R ratio is used to mean the ratio of CO_2 permeability to O_2 permeability, both permeabilities being measured at 20°C unless otherwise noted. Pore sizes given in this specification are measured by mercury porosimetry or an equivalent procedure. Parts and percentages are by weight, except for percentages of gases, which are by volume; temperatures are in degrees Centigrade, and molecular weights are weight average molecular weights expressed in Daltons. For crystalline polymers, the abbreviation T_o is used to mean the onset of melting, the abbreviation T_p is used to mean the crystalline melting point, and the abbreviation ΔH is used to mean the heat of fusion. T_o, T_p and ΔH are measured by means of a differential scanning calorimeter (DSC) at a rate of 10°C/minute and on the second heating cycle. T_o and T_p are measured in the conventional way well known to those skilled in the art. Thus T_p is the temperature at the peak of the DSC curve, and T_o is the temperature at the intersection of the baseline of the DSC peak and the onset line, the onset line being defined as the tangent to the steepest part of the DSC curve below T_p.

The term "enclosure" is used herein to mean a large container (for example a conventional shipping or trucking container, or a conventional ripening room) which is sealed sufficiently to permit a controlled atmosphere to be maintained therein by conventional means well known to those skilled in the art. The term "shipping or trucking container" is used herein to mean a container which has a volume of at least 8 m^3 and which can be loaded onto a ship or a truck. Such containers are well known to those skilled in the art of storing and transporting fruits and vegetables, and are available in a range of standard

sizes. The term "source of exogenous ERA" is used herein to mean a material, object or system which, either immediately or when activated, generates ethylenic ripening agent. The term "latent source of exogenous ERA" is used herein to mean a material, object or system which is generating little or no ERA, but which can be activated so that it generates substantial quantities of exogenous ERA. The term "residue of a source of exogenous ERA" is used herein to mean a material, object or system which is not a part of a fruit and which remains after exogenous ERA has been generated from a source of exogenous ERA. The residue may be for example (i) a solid material which served as a support for exogenous ERA itself or for one or more precursors of exogenous ERA, or (ii) a liquid residue remaining after a solution of a precursor for an ERA, e.g. 2-chloroethyl phosphonic acid, has been used to generate exogenous ethylene and/or a solid residue resulting from the evaporation of solvent from such a solution. The term "residue of exogenous ERA" is used herein to denote a chemical compound which results from the reaction of exogenous ERA with the fruit being ripened (in which case it is optionally part of the ripe fruit) or with another substance within the sealed package. The term "ripening" is used herein to mean increasing ripeness; it includes, but is not limited to and generally does not mean, ripening to a point which results in a product which in a retail store would be sold as "ripe". When applied to fruits which ripen through a climacteric, the term "ripening" means ripening the fruits at least through the climacteric. The term "unripe fruits" is used herein to mean fruits which require ripening before they can be sold in retail stores. When applied to fruits which ripen through a climacteric, the term "unripe fruits" means fruits which have not reached their climacteric. The term "banana" is used herein to include plantains.

Where reference is made herein to sealed packages and sealed containers, and to sealing bags and other containers containing biological materials, it is to be understood that the sealing can be, but generally is not, hermetic sealing. Conventional methods for sealing bags and other containers can conveniently be used in this invention. Such conventional methods include, for example, the use of a cable tie to seal the neck of a polymeric bag. A seal made by conventional methods often is not a hermetic seal, and has the advantage that it permits equilibration of the pressures inside and outside the bag. If the container is sealed hermetically, it will generally be desirable to include one or more pinholes in the container, to achieve such equilibration. The less complete the sealing of the container, the less the influence of the permeability of the container on the packaging atmosphere within it. Thus, even a poor seal may be sufficient, or even desirable, for example when the desired O_2 content of the packaging atmosphere lies between the O_2 content of the atmosphere surrounding the package and the O_2 content of the packaging atmosphere that would result

if the seal was a hermetic seal. Under such circumstances, the sealing could be designed to permit a controlled amount of direct exchange between the packaging atmosphere and the atmosphere surrounding the container.

Control Members

The containers used in the present invention preferably, but not necessarily, include at least one atmosphere control member which provides a pathway for O_2 and CO_2, and which preferably comprises a gas-permeable membrane comprising

(1) a microporous polymeric film, and

(2) a polymeric coating on the microporous film.

The atmosphere control member is preferably a control member as described in one or more of U.S. Patent Nos. 6,013,293 and 6,376,03 and International Publication No. W0 00/04787 incorporated by reference herein. The atmosphere control member or members generally provide at least 50%, preferably at least 75%, of the O_2 permeability of the sealed container.

The microporous polymeric film preferably comprises a network of interconnected pores having an average pore size of less than 0.24 micron, with at least 70% of the pores having a pore size of less than 0.24 micron and at least 80% of the pores having a pore size less than 0.15 micron. Preferably the pores in the microporous film constitute 35 to 80% by volume of the microporous film.

The polymeric coating on the control member preferably comprises a crystalline polymer having a peak melting temperature T_p of -5 to 40 °C., e.g. 0 to 15°C. or 10 to 20°C., an onset of melting temperature T_o such that $(T_p - T_o)$ is less than 10°C., and a heat of fusion of at least 5 J/g. The polymer preferably comprises a side chain crystalline polymer moiety comprising, and optionally consisting of, units derived from (i) at least one n-alkyl acrylate or methacrylate (or equivalent monomer, for example an amide) in which the n-alkyl group contains at least 12 carbon atoms, for example in amount 35-100%, preferably 50-100%, often 80-100%, and optionally (ii) one or more comonomers selected from acrylic acid, methacrylic acid, and esters of acrylic or methacrylic acid in which the esterifying group contains less than 10 carbon atoms. The preferred number of carbon atoms in the alkyl group of the units derived from (i) depends upon the desired melting point of the polymer. For the packaging of biological materials, it is often preferred to use a polymer having a relatively low melting point, for example a polymer in which the alkyl groups in the units derived from (i) contain 12 and/or 14 carbon atoms. The polymer can be a block copolymer in which one of blocks is a crystalline polymer as defined and the other block(s) is crystalline or

amorphous. Preferred block copolymers comprise (i) polysiloxane polymeric blocks, and (ii) crystalline polymeric blocks having a T_p of -5 to 40°C. Such polymers are described in International Publication No. W0 00/24787. Other polymers which can be used to coat the microporous film include cis-polybutadiene, poly (4-methylpentene), polydimethyl siloxane, and ethylene-propylene rubber.

The gas-permeable membrane preferably has one or more of the following properties

- (i) a P_{10} ratio, over at least one 10 °C range between -5 and 15 °C or between 10 and 20 °C. of at least 2.0 to 2.8;
- (ii) an OTR at all temperatures between 20 and 25 °C of 2,480,000 to 7,000,000 ml/m^2.atm.24 hr. (160,000 to 450,000 cc/100 in^2.atm.24hr); and
- (iii) an R ratio of at least 1.3, preferably 2.0, particularly at least 3.0, especially at least 3.5.

The O_2 permeability of the container at 13°C per kilogram of fruits therein (OP13/kg) is preferably at least 700, particularly have least 1000, especially at least 1500, ml/.atm.24hrs. The R ratio of the container at 13°C is preferably at least 1.3, more preferably at least 2, particularly at least 3. The ERA permeability of the container at 13°C per kilogram of fruits therein (ERAP13/kg) is preferably at least 3 times, particularly at least 4 times, the OP13/kg of the container.

The permeability of the container, whether or not it includes an atmosphere control member, can be influenced by perforating the container in order to make a plurality of pinholes therein.

<u>Fruits</u>

This invention is particularly useful for (but is not limited to) the ripening and/or storage of the wide range of fruits which ripen (or undergo other changes, for example, in the case of citrus fruits, de-greening) when exposed to ethylene or another ERA, for example apples, apricots, avocados, bananas, blueberries, cherimoyas, dates, figs, kiwis, mangos, melons, peaches, papayas, pears, peppers, persimmons, and plums (all of which go through a climacteric when they ripen), as well as cherries, grapes, lemons, oranges, tomatoes and strawberries. Some aspects of the invention are especially useful for fruits which in commercial practice are ripened in ethylene-containing ripening rooms, for example avocados, bananas, Bartlett pears, kiwis, mangos, melons, peppers and tomatoes. To

<u>Storage of unripe fruits</u>

When the first area of the invention is being used to store unripe fruits, it is possible to produce desired packaging atmospheres by the selection of containers which, when

sealed around the quantities of fruits in question at the selected storage temperature, have appropriate permeabilities to O_2 and CO_2, and by the selection of an appropriate controlled atmosphere around the sealed packages. Those skilled in the art will have no difficulty, having regard to their own knowledge and the contents of this specification, in making appropriate selections to produce a desired packaging atmosphere or to make a desired compromise between (i) the cost and inconvenience of obtaining an entirely satisfactory combination of container and controlled atmosphere, and (ii) the disadvantage of storing the fruits in a packaging atmosphere which is in some ways unsatisfactory.

The table below sets out, for some of the fruits for which this invention is useful, ranges for the concentrations of O_2 and CO_2 which may be used during storage. The invention is, however, useful, for storing these and other fruits outside the ranges stated in the table below.

Fruit	O_2 content	CO_2 content
Banana	2-5%	3-7%
Tomato	3-5%	2-3%
Kiwi, nectarine, peach	1-2%	3-5%
Fig, blackberry, blueberry, raspberry, strawberry	5-10%	15-20%
Mango, papaya, pineapple	3-5%	5-8%
Avocado	2-5%	3-10%

<u>Ripening unripe fruits by exposure to exogenous ERA</u>

In some embodiment of the invention, unripe fruits are ripened by exposure to exogenous ERA while the fruits are in a sealed container. In some embodiments, the exogenous ERA enters the packaging atmosphere through the container from the atmosphere surrounding the sealed packages, for example as a result of

(i) placing the sealed packages in a conventional ripening room containing exogenous ethylene; or

(ii) generating an exogenous ERA-containing atmosphere around the sealed packages while they are in a large closed container, e.g. a shipping or trucking container, for example by injecting ethylene gas into the container, or by the activation of a source of exogenous ERA which is within the container, but not within the sealed packages; such a source of exogenous ERA could be packed into the container with the sealed packages containing the fruits, for example in the form of packages which release the ripening agent after a desired delay.

In other embodiments, the ERA is generated within each package by activating sources

of exogenous ERA placed individually in the sealed packages of unripe fruits. It is also possible to use a combination of these embodiments.

The amount of ERA in the packaging atmosphere should be sufficient to assist ripening. Thus the packaging atmosphere in each of the sealed packages should generally contain at least 2.5 ppm, preferably at least 20 ppm, typically but not necessarily 100 to 3000 ppm, preferably 250 to 1000 ppm, of ERA. When the exogenous ERA is added to or generated in the atmosphere surrounding the sealed packages, the concentration of ERA in the packaging atmosphere will increase gradually as the exogenous ERA passes through the sealed container, at a rate which depends upon the concentration of ERA in the surrounding atmosphere. If, therefore, a rapid initiation of ripening is desired, the concentration of ERA in the atmosphere surrounding the sealed packages is preferably least 500 ppm, particularly at least 1000 ppm. The table below shows the time taken to reach an ethylene concentration of 100 ppm in the packaging atmosphere of a sealed package of bananas according to the invention, when placed in a ripening room containing the indicated concentrations of ethylene.

Ethylene concentration ppm	100	200	300	400	500	700	1000	1500	2000
Time (hrs.)	5.4	1.5	0.9	0.7	0.5	0.4	0.25	0.2	0.1

An advantage of ripening fruits in a sealed container in accordance with the invention, by comparison with conventional ripening by means of a controlled atmosphere directly in contact with the fruits is that the ripe fruits can be substantially less dehydrated. It is believed that this is because ripening takes place in a more controlled fashion, resulting in lower peak temperatures in the fruits, which in turn results in the reduced dehydration. Thus, bananas typically lose 3 to 5% of their weight between packaging directly after harvest and being put on retail sale. We have found that, through use of the present invention, this weight loss can be substantially reduced, for example to less than 0.5%. Another benefit, when the ripening is carried out below room temperature, is reduced demand on the refrigeration equipment.

The temperature at which ripening is carried out and the concentration of ERA in the packaging atmosphere influence the rate at which ripening takes place. In general, slower ripening results in ripened fruits which remain in a desired range of ripeness for a longer period. On the other hand, rapid ripening may be desired, for example in view of delivery dates required by retail outlets. Thus, the atmosphere around the sealed packages may be above, at, or below ambient temperature. However, it is generally preferred that the

atmosphere should be at a temperature less than 22 °C., preferably less than 21 °C., for example 16-21 °C., or even lower, for example at a temperature less 18 °C. or less than 16 °C., e.g. at 14-15 °C.

The atmosphere within the bags will change substantially during the ripening process, as the ripening fruits consume O_2 and generate CO_2 . The packaging atmosphere, for at least part of the period before ripening fruits reach their climacteric, may contain at least 10%, preferably at least 12%, particularly 14 to 19%, of O_2, and less than 10%, preferably less than 4%, of CO_2, with the total quantity of O_2 and CO_2 being less than 20 %, preferably less than 17 %. For at least part of the period after ripening fruits have passed their climacteric, the packaging atmosphere may contain at least 0.8%, for example 1.5 to 6% or 1.5 to 3%, of O_2, and less than 15%, preferably less than 7%, of CO_2, with the total quantity of O_2 and CO_2 being less than 16%, preferably less than 10 %.

When it is desired to ripen fruits while they are being transported, for example on a ship or a truck, ripening by means of a source of exogenous ERA placed within the sealed packages and/or by means of a source of exogenous ERA placed within a large enclosure containing the sealed packages, is particularly useful. The ripening can be preceded by a storage period in which there is little or no ripening. The ripening and optional storage process can be controlled so that the fruits are at a desired state of ripeness when they reach their destination. During the process, there may be no need to alter the controlled atmosphere around the sealed packages. However, when the fruits are stored before they are ripened, it may be desirable to restrict the amount of oxygen which enters the sealed packages during storage, in order to prevent or delay ripening. When the packages can be surrounded by a controlled atmosphere (for example while being transported in the hold of a suitably equipped ship), this result can be achieved by placing the sealed packages in a controlled atmosphere containing less than the amount of oxygen present in air (about 21 %), for example less than about 12%. The source of exogenous ERA can make ERA available immediately after packaging the bananas, or after a desired delay. Delayed release of ERA can result, for example, from the use of an exogenous to ERA source which (i) is activated by an increase in moisture content (for example by water which reaches the ERA source as a result of capillary wicking of water through an intermediate body which separates a water reservoir from the ERA source), or (ii) is associated with (e.g. surrounded by or adsorbed onto) a material which releases ERA or one or more precursors for an ERA, after a set time or in response to some outside intervention, for example an increase in temperature.

Any convenient source of exogenous ERA can be used. We have obtained good results using 2-chloroethyl phosphonic acid, which is often referred to herein as 2CPA. 2CPA can be used in the form of an aqueous solution, for example of concentration 3-4%. The rate at which 2CPA generates ethylene increases with increasing pH of the aqueous solution, which can be adjusted, for example to more than 4, particularly more than 7, by the addition of suitable materials, for example buffer solutions and/or sodium bicarbonate solutions. In one embodiment, a 2CPA solution and a pH adjuster are adsorbed on the same or different absorbent pads, e.g. paper pads, and the pad(s) placed in the bottom of the bag and covered with a polymeric sheet before the unripe fruits are placed in the containers. In another embodiment, a solution of 2CPA is applied to the unripe fruits, for example by dipping or spraying, before they are placed in the bag. The invention also includes the possibility that ripe fruits are the source of exogenous ERA, the ripe fruits generating ethylene and being of the same family as, or a different family from, the unripe fruits which are to be ripened. For example, for ripening green bananas, the source of exogenous ERA could be a perforated container containing apples or bananas which have passed their climacteric.

As in the aspects of the invention which involve ripening in an exogenous ERA-containing atmosphere surrounding the sealed packages, the atmosphere within sealed bags containing a source of exogenous ERA will change during the ripening process. The packaging atmospheres, for at least part of the periods before and after the climacteric, are preferably as stated above when the sealed bags are surrounded by an exogenous ERA-containing atmosphere.

<u>Quantities of fruits</u>

The invention can in principle be used for any quantity of fruits. In some embodiments, the sealed container preferably contains at least 4 kg, particularly at least 15 kg, especially 16 to 22 kg of fruits. In other embodiments, smaller quantities are used.

EXAMPLE

The invention is illustrated in the following Example. In the Example, the Type S control members were as described in International Publication No. WO 00/04787 and comprised a microporous polyethylene film coated with a polysiloxane/SCC block copolymer. The Type S members had an OTR at 13 °C of about 3,803,850 (245,410) and at 22 °C of about 5,000,000 (324,000), an EtTR at 13 °C of about 16,280,000 (1,050,300) and at 22 °C of about 19,500,000 (1,260,000), an R ratio of about 3.8, and a P10 ratio (between 0 and 10 °C.) of about 1.8. The microporous polyethylene film contained 50-60% silica, had

a thickness of about 0.18 mm (0.007 inch), a tear strength of about 90g, a porosity of about 65%, an average pore size of about 0.1 micron and a largest pore size of 4-10 microns (available from PPG industries under the tradename Teslin SP 7). The block copolymer was prepared by the reaction of a polydimethyl siloxane terminated one end only by a methacryloxypropyl group (available from Gelest under the tradename MCR M17), 40 parts, dodecyl acrylate, 26.8 parts and tetradecyl acrylate, 33.2 parts, as described in Example A7 of International Publication No. WO 00/04787.

The color stages referred to in the Example are those accepted by the industry and as shown below.

Color stage	Description
1	95% green
2	80% green, 20% slightly yellow
3	50% yellow, 50% green
4	80% yellow, 20% light green
5	95% yellow, with slight green color at stem and blossom end
6	100% yellow
7	100% yellow with brown sugar spots

<u>Example</u>

Three trials were carried out to compare the weight loss of Cavendish bananas transported from Columbia and ripened (a) conventionally in 12 conventional bags as controls, and (b) in accordance with the invention in 36 bags having atmosphere control members. Each bag was supported by a cardboard box. The conventional bags were about 1 m. (38.5 in.) by 1.25 m. (49.5 in.) and were made of polyethylene film about 0.18 mm (0.0007 in.) thick. Each conventional bag was perforated with about 312 holes, each about 12.5 mm (0.5 inch) in diameter. The bags used in accordance with the invention were about 1 m. (39.75 in.) by 1.2 m (46.25 in.) and were made of a film of a blend of polyethylene and ethylene/vinyl acetate copolymer about 0.05 mm (0.002 in.) thick. Each bag had two S-type atmosphere control members, each control member being about 145 mm (5.625 in.) by 120 mm (4.72 in.) and being secured to the exterior of the bag by a layer of contact adhesive about 11 mm (0.44 in.) wide around its periphery. Under each atmosphere control member, the bag had seven holes each about 25 mm (1 in.) in diameter. The effective area of the control member was about equal to the area of the holes in the bag.

In Columbia, each bag was packed with about 20 kg. of green, freshly harvested bananas. The necks of the bags of the invention were sealed with rubber bands. The necks of the conventional bags were not closed. The bags were weighed and then transported at about 14.5 °C (58 °F) to Watsonville, California, U.S.A., where, 13 days after harvest, they were placed in a commercial ripening room containing ethylene for 24 hours at about 16.5 °C (62 °F). The room was then vented and maintained at about 16.5 °C (62 °F) for the next 24 hours, at about 15.5 °C (60 °F) for the next 48 hours, and at about 14.5 °C (58 °F) for the next 24 hours. The bananas were then maintained at about 21 °C (70 °F). The table below shows the average weight loss of the bags, and the color of the bananas in the bags, on the day indicated. The sealed bags were not opened until the day indicated in the table below.

	Trial 1		Trial 2		Trial 3	
	Invention	Control	Invention	Control	Invention	Control
Days after harvest	11	9	10	9	10	9
Weight loss (%)	0.44	5.17	0.4	4.6	0.07	4.66
Color	5.25	7	5.75	9	5.3	7

The results reported in this table show clearly that the practice of the invention results in bananas which lose less weight through dehydration and which remain at a desired color stage for a longer time.

Claims

1. A method of treating, e.g. storing and/or ripening, a respiring biological material, the method comprising

(A) providing a sealed package comprising

(a) a sealed container, and

(b) within the sealed container, the respiring biological material and a packaging atmosphere around the respiring biological material;

the sealed container providing a pathway for O_2 and CO_2 to enter or leave the packaging atmosphere;

(B) exposing the exterior of the sealed package to a first controlled atmosphere;

(C) after step (B), exposing the exterior of the sealed package to a second controlled atmosphere;

the difference between the O_2 contents of the first and second controlled atmospheres being at least 1%, preferably at least 3%.

2. A method according to Claim 1 wherein one of the first and second controlled atmospheres is air.

3. A method according to Claim 1 or 2 wherein

(a) in step (B), the first controlled atmosphere has an O_2 content which is (i) less than 18% O_2, preferably less than 12% O_2, particularly less than 9% O_2, and (ii) more than 2% O_2, preferably more than 4% O_2, particularly more than 5% O_2, and

(b) in step (C), the second controlled atmosphere contains at least 3% more O_2 than the first atmosphere.

4. A method according to any one of claims 1 to 3 wherein

(a) at the beginning of step (B), the fruits are unripe fruits which ripen when exposed to an ethylenic ripening agent (ERA), for example green bananas

(b) the O_2 content of the first controlled atmosphere and the permeability of the container are such that the O_2 content of the packaging atmosphere during step (B) is high enough to maintain respiration of the unripe fruits and low enough that the unripe fruits ripen slowly or not at all; and

(c) the second controlled atmosphere contains exogenous ERA.

5. A method according to Claim 1 or 2

(a) at the beginning of step (B), the fruits are unripe fruits which can be ripened by exposure to ethylene, for example green bananas;

(b) during at least part of step (B), the first controlled atmosphere contains at least 23% O_2, preferably 25-30% O_2, e.g. about 28% O_2, and exogenous ERA, for example at least 20 ppm, e.g. 100 to 3000 ppm, of ethylene; and

(c) during at least part of step (C), the second controlled atmosphere contains 18 to 22% O_2 , for example is air.

6. A method according to Claim 5 wherein the O_2 content of the packaging atmosphere is 4 to 8%, preferably 5.5 to 6.5%, during at least part of step (B), and 2 to 4%, preferably 2.5 to 3.5%, during at least part of step (C).

7. A method according to any one of claims 1 to 5 wherein

(a) the fruits are bananas which are green at the beginning of step (B);

(b) the sealed container contains a latent source of exogenous ERA;

(c) at least the initial parts of step (B) is carried out under conditions such that ERA is not released from the latent source; and

(d) during or after step (B), the latent source of exogenous ERA is activated, thereby releasing exogenous ERA which ripens the bananas.

8. A method according to Claim 6 or 7 wherein the sealed container consists essentially of a polyethylene bag.

9. A method according to any one of claims 1 to 7 wherein the container includes at least one atmosphere control member which provides a pathway for O_2 and CO_2 to enter or leave the packaging atmosphere and which comprises a gas-permeable membrane comprising

(i) a microporous polymeric film, and

(ii) a polymeric coating on the microporous film.

10. A method according to any one of Claim 6 to 9 wherein

(a) the second controlled atmosphere contains (i) less than 18% O_2, preferably less than 12% O_2, particularly less than 9% O_2, and (ii) more than 2% O_2, preferably more than 4% O_2, particularly more than 5% O_2; and

(b) has an O_2 permeability such that, during at least one period of step (B), the O_2 content of the packaging atmosphere reaches a value which is (i) more than 1%, preferably more than 2%, and (ii) less than 7%, preferably less than 5%, particularly less than 3.5%.

11. A container system suitable for carrying out the method of any one of claims 1 to 10 or which has been used to carry out the method of any one of claims 1 to 10, the system comprising

(1) a sealed enclosure having an inlet port;

(2) within the enclosure, a plurality of sealed packages, each of which comprises

(a) a sealed container, and

(b) within the sealed container, a respiring biological material and a packaging atmosphere around the respiring biological material,

the sealed container providing a pathway for O_2 and CO_2 to enter or leave the packaging atmosphere; and

(3) a source of O_2 connected to the inlet port, whereby the sealed packages can be surrounded by a controlled atmosphere having a desired O_2 content.

12. A container system according to Claim 11 wherein the sealed enclosure is (1) a shipping or trucking container, or (2) a ripening room.

13. A container system according to Claim 11 or 12 wherein the respiring material is bananas.

14. A container system according to any one of claims 11 to 13 wherein

(a) the sealed enclosure includes a second inlet port and a source of exogenous ERA connected to the second inlet port, or

(b) within the sealed enclosure there is a latent source of exogenous ERA, or a source of exogenous ERA, or the residue of a source of exogenous ERA.

15. A package which comprises

(a) a sealed container, and

(c) within the sealed container, (i) unripe fruits which can be ripened by exposure to an ethylenic ripening agent (ERA), (ii) a packaging atmosphere around the unripe fruits, and (iii) a latent source of ERA or a source of ERA.

16. A package according to Claim 15 wherein the sealed container has an O_2 permeability at 13 °C, per kg of fruits in the container (OP13/kg), of at least 700, preferably at least 1000, particularly at least 1500, ml/atm.24 hrs, an R ratio at 13 °C of at least 2, preferably at least 3, and an ERA permeability at 13 °C, per kg of bananas in the container (ERAP13/kg) which is at least 2 times, preferably at least 4 times, the OP13/kg of the container.

17. A package according to Claim 15 or 16 wherein the container includes at least one atmosphere control member which provides a pathway for O_2, CO_2 and ethylene to enter or leave the packaging atmosphere and which comprises a gas-permeable membrane comprising

(a) a microporous polymeric film, and

(b) a polymeric coating on the microporous film;

the gas-permeable membrane having an oxygen permeability (OTR), at all temperatures between 20 and 25ºC, preferably at all temperatures between 13 and 25°C, of at least 775,000 ml/m^2.atm.24 hrs (50,000 cc/100 inch^2.atm.24 hrs), preferably at least 2,480,000 ml/m^2.atm.24 hrs (160,000 cc/100 inch^2.atm.24 hrs), e.g. 2,480,000 to 7,000,000 ml/m^2.atm.24 hrs (160,000 to 450,000 cc/100 inch^2.atm.24 hrs).

18. A method of ripening unripe fruits which comprises

(A) providing a sealed package as claimed in any one of claims 15 to 17, and

(B) exposing the unripe fruits in the sealed package to ERA from the source of ERA in the sealed container.

19. A method of ripening unripe fruits which comprises

(A) providing a package which comprises

(a) a sealed container, and

(b) within the sealed container, unripe fruits which can be ripened by exposure to an ethylenic ripening agent (ERA), and a packaging atmosphere around the unripe fruits,

the sealed container having an O_2 permeability at 13 °C, per kg of fruits in the container (OP13/kg), of at least 700, preferably at least 1000, particularly at least 1500, ml/atm.24 hrs, an R ratio at 13 °C of at least 2, preferably at least 3, and an ERA permeability at 13 °C, per kg of fruits in the container (ERAP13/kg) which is at least 2 times, preferably at least 4 times, the OP13/kg of the container, and

(B) placing the sealed package in an atmosphere containing ERA.

20. A method according to Claim 19 wherein step (B) comprises placing the sealed package in a ripening room containing ethylene, preferably in amount at least 20 ppm, for example 500 to 1000 ppm.

21. A method according to Claim 19 or 20 wherein at least part of step (B) is carried out at a temperature less than 22 °C, preferably less than 20 °C, for example at 16-21°C.

22. A sealed package which comprises

(a) a sealed container, and

(b) within the sealed container, (i) fruits, for example fruits which have ripened through a climacteric, (ii) a packaging atmosphere around the fruits, and (iii) exogenous ERA and/or a residue of exogenous ERA and/or the residue of a source of exogenous ERA, the exogenous ERA and/or residue of exogenous ERA optionally being a gas which is part of the packaging atmosphere;

the sealed container providing a pathway for O_2, CO_2 and ERA to enter or leave the packaging atmosphere.

23. A package which comprises

(a) a container, the container being a sealed container or an open container obtained by opening a sealed container, and

(b) within the container, (i) fruits, and (ii) a packaging atmosphere around the fruits; the container, if it is sealed, providing a pathway for O_2, CO_2 and ERA to enter or leave the packaging atmosphere, and if it is open, having provided a pathway for O_2, CO_2 and ERA to enter or leave the packaging atmosphere when it was sealed; the container having one or both of the following characteristics

(i) the fruits therein have been ripened at least in part by exposure to exogenous ERA, and

(ii) it contains the residue of a source of exogenous ERA.

24. An enclosure, for example a shipping or trucking container or a ripening room, which contains a plurality of sealed packages, each of the packages comprising

(a) a sealed container, and

(b) within the sealed container, (i) fruits, for example fruits which have ripened through a climacteric, or unripe fruits which ripen through a climacteric, and (ii) a packaging atmosphere around the fruits;

the sealed container providing a pathway for O_2, CO_2 and ERA to enter or leave the packaging atmosphere;

the enclosure containing the plurality of sealed packages having at least one of the following features

(i) the packaging atmosphere in each of the sealed packages contains exogenous ERA;

(ii) at least some, and preferably each, of the sealed packages contains and exogenous ERA and/or a residue of exogenous ERA, the exogenous ERA and/or residue of exogenous ERA optionally being a gas which is part of the packaging atmosphere, or

(iii) the enclosure contains not only the sealed packages containing the fruits but also, not within any of the sealed packages, exogenous ERA and/or a residue of exogenous ERA, the exogenous ERA and/or residue of exogenous ERA optionally being a gas which is part of the atmosphere which contacts the exterior of the sealed packages.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/37199

A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A23B A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 799 495 A (GAST JR WILLIAM A ET AL) 1 September 1998 (1998-09-01) claims 9,1; figures ---	1-24
X	WO 95 00030 A (CHIQUITA BRANDS INC) 5 January 1995 (1995-01-05) page 5, line 17 - line 25; claims 1,23,39-42; figures ---	1-24
X	US 5 667 827 A (BREEN DENNIS J ET AL) 16 September 1997 (1997-09-16) claims; figures ---	1,2
X	US 5 711 978 A (BREEN DENNIS J ET AL) 27 January 1998 (1998-01-27) claims; figures ---	1,2
	-/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° *Special categories of cited documents :*

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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